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MEMORANDUM FOR IN-HOUSE PUBLICATIONS

FROM: PROI (TI) (STINFO) 30 Apr 98

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-**TP**-1998-099
Christe (Raytheon) Boatz, Sheehy "Theory and Synthesis of New High Energy Density Materials"
HEDM Conference Presentation **(Statement A)**

appropriateness of distribution

THEORY AND SYNTHESIS OF NEW HIGH ENERGY DENSITY MATERIALS

Karl O. Christe, William W. Wilson, Greg W. Drake, Jeff A. Sheehy, Jerry A. Boatz, Berthold Hoge, Ross I. Wagner, and Xiongzhi Zhang
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Efforts are described to combine the NF_4^+ cation with highly energetic anions, such as NO_2^-, NO_3^-, and $N(NO_2)_2^-$. In the case of NO_3^-, the NO_3^- anion was fluorinated already at very low temperatures by NF_4^+ to give fluorine nitrate in high yield. In the case of NO_2^-, the reaction with NF_4^+ yielded an unknown unstable decomposition product in low yield, but the reaction was very difficult to control and consistently exploded. In the case of $N(NO_2)_2^-$, again no stable salt was formed, and a thermally unstable decomposition product, probably $FN(NO_2)_2$, was observed by ^{19}F NMR spectroscopy.

In search for new difluoroaminating agents, attempts were made to prepare $SO_2(NF_2)_2$ from N_2F_4 and either SO_2 or SO_2Cl_2 using thermal or photholytic methods. Only the previously known compounds, FSO_2NF_2 and $ClSO_2NF_2$, were obtained.

The possibility of stabilizing ozone by protonation in superacid solution was investigated. It was found that ozone does not form a stable O_3H^+ cation at temperatures as low as -78 C.

The synthesis and reactions of oxidative oxygenators, which might lead to the novel oxidizer ClF_5O, were explored. It was found that HOF does not oxygenate ClF_3, ClF_3O, BrF_5 or IF_5. Attempts to repeat a previously reported synthesis of H_2OF^+ salts from XeF^+ and water, which had been claimed to be cabable of oxygenating ClF_3 to ClF_3O, revealed that the previous claims are incorrect. No evidence for the existence of H_2OF^+ salts was found. Instead a novel oxygen bridged water adduct of XeF^+ is formed in these systems. When reacted with ClF_3, this adduct forms ClO_2^+ salts and not ClF_2O^+ salts, as previously claimed.

The $ClF_4^+SbF_6^-$ and $O_2^+SbF_6^-$ salts were prepared and their crystal structure were determined.

In the area of high coordination number compounds, our studies of the pentagonal planar IF_5^{2-} anion and the pentagonal bipyramidal SbF_7^{2-} and BiF_7^{2-} anions were completed and written up in manuscript form.

Extensive use of electronic structure calculations was made in these studies to determine the geometries, stabilities, vibrational and NMR spectra of these molecules.

THEORY AND SYNTHESIS OF NEW HIGH ENERGY DENSITY MATERIALS

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NF_4^+ CHEMISTRY

- NF_4^+ CATION FIRST PREPARED IN 1965 BY US AT STAUFFER AS $NF_4^+AsF_6^-$ SALT
- HIGHLY ENERGETIC CATION WHICH IS STABLE UP TO 250 °C
- $NF_4^+BF_4^-$ HAS BEEN USED FOR DEVELOPMENT OF SOLID PROPELLANT NF_3/F_2 GAS GENERATORS FOR CHEMICAL HF/DF LASERS
- FOR ROCKET PROPULSION OR EXPLOSIVES APPLICATIONS, AN ENERGETIC COUNTERION IS REQUIRED
- THE ONLY ENERGETIC NF_4^+ SALT PREPARED SO FAR:
  $NF_4^+ClO_4^-$ (CHRISTE, WILSON, INORG. CHEM. 1980)
  BUT IS THERMALLY UNSTABLE

NF_4^+ CHEMISTRY

- ENERGETIC NF_4^+ SALTS OF INTEREST

  $NF_4^+ NO_3^-$

  $NF_4^+ NO_2^-$

  $NF_4^+ N(NO_2)_2^-$

- SYNTHESIS BY METATHESIS

$$NF_4^+SbF_6^- + Cs^+NO_3^- \xrightarrow[L.T.]{\text{SOLVENT}} CsSbF_6\downarrow + NF_4^+NO_3^-$$

- PROBLEM: HF SOLVENT REACTS WITH NO_3^-

$$NO_3^- + 4HF \xrightarrow{HF} NO_2^+ + 2HF_2^- + H_2O$$

- ANSWER: USE SO_2 OR CH_3CN AS SOLVENTS

$NF_4^+NO_3^-$

$$NF_4^+SbF_6^- + Cs^+NO_3^- \xrightarrow[-78^\circ C]{SO_2} CsSbF_6\downarrow + [NF_4^+NO_3^-]$$

$$[NF_4^+NO_3^-] \xrightarrow{-78^\circ C} NF_3 + FONO_2$$

- NF_4NO_3 IS THERMALLY VERY UNSTABLE
- NEW SYNTHESIS OF $FONO_2$ IN QUANTITATIVE YIELD

NF_4^+/NO_2^- SYSTEM

- REACTION OF $NF_4^+SbF_6^-$ + $K^+NO_2^-$ IN CH_3CN SOLUTION IS VIOLENT
- OBSERVED A NEW, UNSTABLE COMPOUND WITH STRONG IR BANDS AT

1871 cm^{-1}	TERMINAL N=O STRETCH
1185 cm^{-1}	N-O STRETCH OR ν_{asym} F-O-N
832 cm^{-1}	O-F STRETCH OR ν_{sym} F-O-N

- MOST LIKELY COMPOUND: "FONO", HOWEVER:
  - PREVIOUS MATRIX ISOLATION STUDY BY SMARDZEWSKI (1974) PROPOSED 1716, 1199, 702 cm^{-1} FOR FONO
  - AB INITIO CALCULATIONS (SHEEHY, LEE, DIXON, SORENSON) DO NOT FIT WELL FOR EITHER DATA SET (PROBLEM CASE!)

$NF_4^+/N(NO_2)_2^-$ SYSTEM

- LOW-TEMPERATURE ^{19}F NMR STUDY OF

$$NF_4^+SbF_6^- + Cs^+N(NO_2)_2^- \xrightarrow[-75\ TO\ -25^\circ C]{SO_2} CsSbF_6\downarrow + NF_4^+N(NO_2)_2^-$$

  - SHOWED $NF_4^+N(NO_2)_2^-$ TO BE STABLE BELOW $-50^\circ C$
  - ABOVE $-50^\circ C$, NF_3 EVOLUTION AND FORMATION OF A THERMALLY UNSTABLE COMPOUND WITH $S = 53.3$
  - AB INITIO CALCULATIONS FOR $FN(NO_2)_2$ GIVE $S = 53.9$ (IGLO II, B3LYP/6-31G*)

- FT-IR STUDY OF GASEOUS DECOMPOSITION PRODUCTS FROM $NF_4^+SbF_6^- + K^+N(NO_2)_2^-$ REACTION IN HF AT $-78^\circ C$ SHOW NEW BANDS AT 1711, 1324, 1301, 878, 803, 458 cm^{-1}, IN ACCORD WITH EXPECTATIONS FOR $FN(NO_2)_2$
- MORE COMPLETE CHARACTERIZATION AND THEORETICAL CALCULATIONS ARE IN PROGRESS

WORK IN PROGRESS ON NOVEL NF_2 HEDM COMPOUNDS

- NF_2OClO_3

$$NF_2OSO_2F + Cs^+ClO_4^- \longrightarrow Cs^+SO_3F^- + NF_2OClO_3$$

- $SO_2(NF_2)_2$ ("BAUM REAGENT")

$$SO_2 + N_2F_4 \xrightarrow{UV \text{ or } \Delta T} FSO_2NF_2 \text{, BUT NOT } SO_2(NF_2)_2$$

$$SO_2Cl_2 + N_2F_4 \xrightarrow{UV \text{ or } \Delta T} ClSO_2NF_2 \text{, BUT NOT } SO_2(NF_2)_2$$

$$SF_5NF_2 + K^+N(NO_2)_2^- \not\longrightarrow FSO_2NF_2$$

$$\left(SF_4(NF_2)_2 \longrightarrow SO_2(NF_2)_2 \right)$$

- BAUM REAGENT IS NOT $SO_2(NF_2)_2$, VIBRATIONAL SPECTRA AND PHYSICAL PROPERTIES SUGGEST $NF_2SO_2\text{-}O\text{-}SO_2NF_2 \cdot nSO_3$

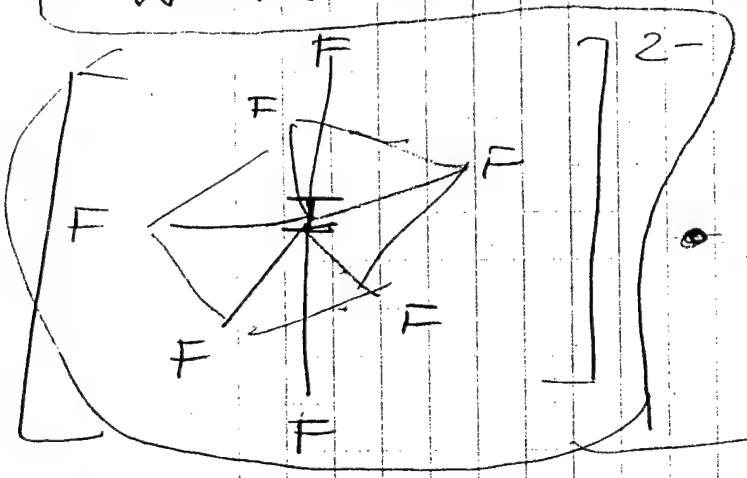
STABILIZATION OF OZONE

- O_3 IS 34.1 kcal/mol ENDOTHERMIC
- I_{sp} OF O_3/H_2 IS 39 sec HIGHER THAN O_2/H_2
- O_3H^+ HAS BEEN OBSERVED BY ION CYCLOTRON RESONANCE SPECTROSCOPY (CACACE, 1994)
- SHOCK SENSITIVE O_3 MIGHT BE STABILIZED BY PROTONATION

- $O_3 + HF + SbF_5 \xrightarrow[HF]{-78^\circ C}$ LITTLE SOLUBILITY OF O_3 IN LIQUID PHASE, RESULTING IN SEPARATE PURE O_3 PHASE AT -196

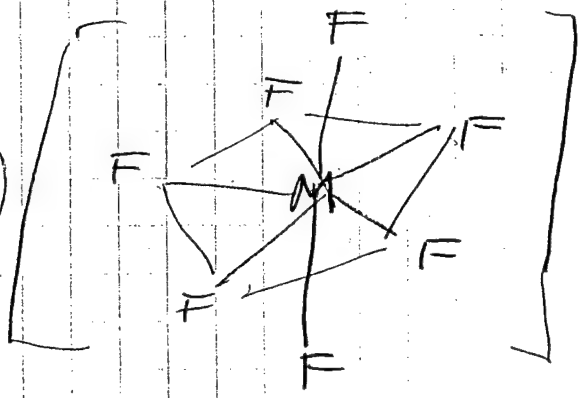
CHEMISTRY AT THE LIMITS OF COORDINATION

- WORK ON PENTAGONAL PLANAR IF_5^{2-} WAS COMPLETED AND PUBLISHED IN JACS (MAY 9



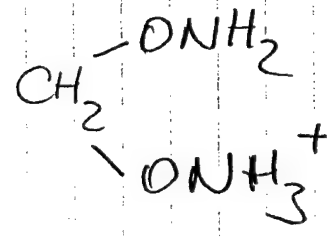
- XeF_5^- AND IF_5^{2-} ARE THE ONLY KNOWN PENTAGONAL PLANAR SPECIE

- WORK ON SbF_7^{2-} AND BiF_7^{2-} WAS ALSO COMPLETED AND IS IN PRESS (JACS)



- ALTHOUGH SbF_6^- AND BiF_6^- HAD BEEN KNOWN FOR A VERY LONG TIME, SbF_7^{2-} AND BiF_7^{2-} HAD BEEN UNKNOWN

CRYSTAL STRUCTURE DETERMINATIONS.

- $ClF_4^+ SbF_6^-$
- $O_2^+ SbF_6^-$
- $OH_3^+ SbF_6^-$
- $N_2F_3^+ Sb_2F_{11}^-$
-  $C(NO_2)_3^-$

ClF_5O

- ClF_5O WOULD BE HIGHEST ~~PERFORMING~~, EARTH-STORABLE OXIDIZER WITH AN I_{sp} BEING 10 sec HIGHER THAN THAT OF C
- THEORETICAL CALCULATIONS SHOW THAT IT IS VIBRATIONALLY STABLE
- ALL PREVIOUS ATTEMPTS TO OXIDATIVELY FLUORINAT ClF_3O OR ClF_4O^- FAILED DUE TO OXIDATIVE ATTACK ON OXYGEN

  EXAMPLE: $ClF_3O + KrF^+ \longrightarrow ClF_4^+ + \frac{1}{2}O_2$

- ALTERNATE POTENTIAL ROUTE TO ClF_5O

  OXIDATIVE OXYGENATION OF ClF_5

  ClF_5 + "MAGIC OXYGENATOR" $\longrightarrow$ ClF_5O

"MAGIC OXYGENATOR"

- MINKWITZ, NOWICKI (ANGEW. CHEMIE, 1990)

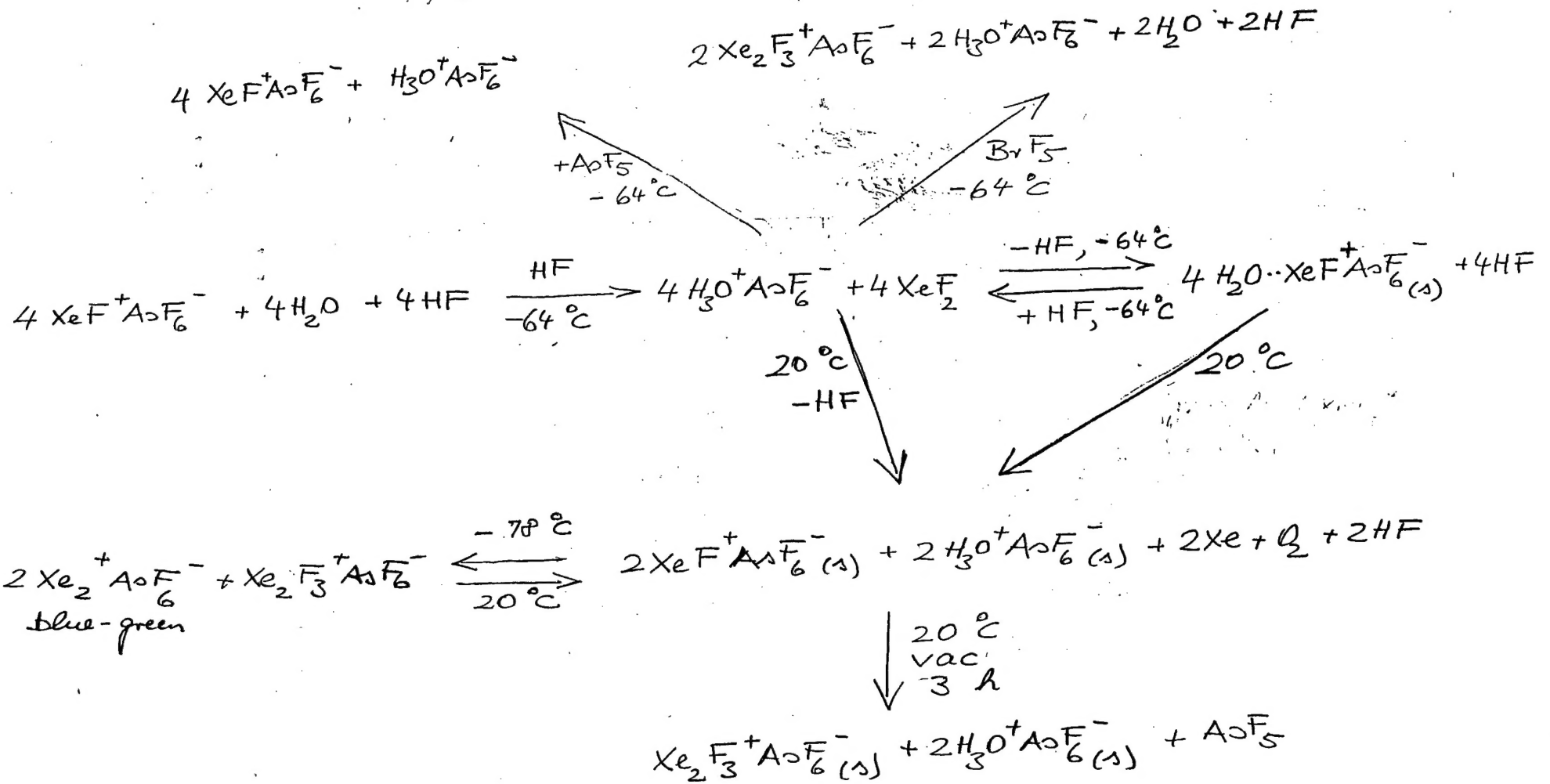
$$XeF^+MF_6^- + H_2O \xrightarrow[-60\,^\circ C]{HF} H_2OF^+MF_6^-$$

(M = As, Sb)

$$H_2OF^+MF_6^- + CeF_3 \xrightarrow{HF} CeF_2O^+MF_6^- + 2HF$$

- OUR RESULTS
  - XeF^+/H_2O SYSTEM IS EXTREMELY COMPLEX, BUT DOES NOT GIVE H_2OF^+ SALTS
  - XeF^+/H_2O REACTION PRODUCT DOES NOT OXYGENATE CeF_3, BUT HYDROLYSES IT TO CeO_2^+
  - WORK IN PROGRESS TO FULLY CHARACTERIZE THIS SYSTEM BY:
    - VIBRATIONAL AND MULTINUCLEAR NMR SPECTROSCO
    - SINGLE CRYSTAL X-RAY DIFFRACTION
    - COMPUTATIONAL CHEMISTRY

$XeF^+AsF_6^-/H_2O$ SYSTEM



$$FXe\cdot\cdot OH_2^+\,AsF_6^- + XeF_2 \xrightarrow{-HF} \left[FXe\text{-}\overset{H}{O}\text{-}XeF\right]^+AsF_6^- \xrightarrow[-AsF_5]{-HF} FXe\text{-}O\text{-}XeF$$

HOF REACTIONS

- PREPARATION

$$F_2 + H_2O \xrightarrow{-45\,^\circ C} HOF + HF$$

- PROTONATION

$$HOF + HF + SbF_5 \xrightarrow[-78\,^\circ C]{HF} \text{DOES NOT GIVE } H_2OF^+SbF_6^-$$

- REACTION CHEMISTRY
  - REACTIONS OF HOF WITH CeF_3, CeF_3O, CeF_5, BrF_5 OR IF_5 WERE STUDIED IN GASPHASE BY FT IR SPECTROSCOP
  - NO EVIDENCE FOR OXIDATIVE OXYGENATIONS

PUBLICATIONS DURING LAST YEAR

1) NAKED FLUORIDE ION SOURCES (JACS)

2) TETRAFLUOROPHOSPHATE ANION, POF_4^- (JACS)

3) DISORDER AND POLYMORPHISM IN $N(CH_3)_4IO_4$ (INORG. CHEM)

4) PREPARATION, NMR, RAMAN AND DFT/IGLO/GIAO-MP2 STUDY OF MONO-, DI-, AND TRI-PROTONATED THIOUREA (JACS)

5) ^{17}O AND ^{13}C NMR/AB INITIO STUDY OF OXONIUM AND CARBOXONIUM IONS (JACS)

6) DIRECT SYNTHESES OF $N(CH_3)_4^+$ SALTS OF COMPLEX FLUOROANIONS (J. FLUOR. CHEM.)

7) NOVEL HEDM MATERIALS. SYNTHESIS AND CHARACTERIZATION OF $C(N_3)_3^+$ SALTS OF $N(NO_2)_2^-$, ClO_4^- AND BF_4^- (JACS)

8) TRIMETHYL PEROXONIUM ION, $CH_3OO(CH_3)_2^+$ (JACS)

9) THEORETICAL STUDY OF NO_4^+ (J. PHYS. CHEM)

10) PENTAGONAL PLANAR AX_5 SPECIES, IF_5^{2-} (JACS)

11) PREPARATION AND VIBRATIONAL SPECTRA OF $N(CH_3)_4^+IF_2^-$ AND ELECTRONIC STRUCTURE CALCULATIONS OF IF_2^-, BrF_2^-, ClF^-, XeF AND KrF (J. FLU

SUMMARY

- THE COMBINATION OF NF_4^+ WITH THE ENERGETIC ANIONS NO_3^-, NO_2^- AND $N(NO_2)_2^-$ YIELDS THERMALLY UNSTABLE MATERIALS WHICH DECOMPOSE TO $FONO_2$ AND INTERESTING NEW COMPOUNDS, TENTATIVELY IDENTIFIED AS FONO AND $FN(NO_2)_2$
- IN SEARCH FOR NOVEL NF_2 SUBSTITUTED OXIDIZERS AND DIFLUOROAMINATING REAGENTS, THE SYNTHESES OF NF_2OCO_3 AND $SO_2(NF_2)_2$ WERE PURSUED
- OZONE CANNOT BE STABILIZED THROUGH PROTONATION
- IN PURSUIT OF CF_5O, A NEW LIQUID EARTH-STORABLE OXIDIZER, THE PREVIOUSLY REPORTED H_2OF^+ CATION AND ITS ALLEGED OXYDATIVE OXYGENATING POWER COULD NOT BE CONFIRMED. THE REPORTED H_2OF^+ SALTS ARE ACTUALLY $[FXe{-}{-}OH_2]^+$ ADDUCTS.
- THE CRYSTAL STRUCTURES OF NUMEROUS HEDM COMPOUNDS WERE DETERMINED
- WORK WAS COMPLETED ON THE PENTAGONAL PLANAR IF_5^{2-} AND PENTAGONAL BIPYRAMIDAL SbF_7^{2-} AND BiF_7^{2-} ANIONS
- THIS PROGRAM CONTINUES TO BE A SHOWCASE FOR THE SYNERGISM BETWEEN THEORY AND SYNTHESIS AND HAS PRODUCED 11 HIGH QUALITY PUBLICATIONS DURING THE PAST YEAR